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Formation of Well-defined Nanocolumns by Ion Tracking Lithography

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Abstract

Low dimensional systems on the nanometer scale afford a wealth of interesting possibilities including highly anisotropic behavior and quantum effects. Nanocolumns permit electrical and mechanical contact, yet benefit from two confined dimensions. This confinement leads to new optical, mechanical, electrical, chemical, and magnetic properties. We construct nanocolumn arrays with precise definition and independent control of diameter, length, orientation, areal density and composition so that geometry can be directly correlated to the quantum physical property of interest. The precision and control are products of the fabrication technique that we use. The process starts with an ion of sufficient energy to "track" a dielectric such as a film applied uniformly onto a substrate. The energy loss of the ion alters chemical bonding in the dielectric along the ion's straight trajectory. A suitable etchant quickly dissolves the latent tracks leaving high aspect ratio holes of small diameter (~10nm) penetrating a film as thick as several microns. These small holes are interesting and useful in their own right and can be made to any desired size by continuing the etching process. Moreover, they serve as molds for electrochemical filling. After this electro-deposition, the mold material can be removed leaving the columns firmly attached to the substrate at the desired orientation. A variety of structures can be envisioned with these techniques. As examples, we have created arrays of Ni and of Pt nanocolumns (~ 60 nm diameter and ~ 600 nm long) oriented perpendicular to the substrate. The high aspect ratio and small diameter of the columns enables easy observation of quantum behavior, namely efficient electron field emission and Fowler Nordheim behavior.

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Introduction

Low dimensional systems on the nanoscale have attracted attention recently due to their ability to exhibit quantum size effects [1]. Films sufficiently thin can exhibit such effects, but small grain size usually interferes [2,3]. Nanodots are well known to show strong quantum effects, but conventional contacts and interfaces are of course impossible – thus limiting experimental testing and technological utility. Nanowires (more generally nanocolumns, to stress that nonmetals are of interest as well) permit electrical and mechanical contact – yet benefit from two confined dimensions. This confinement leads to new optical, mechanical, electrical, chemical, and magnetic properties. Eventual applications for arrays of nanocolumns may develop in opto-electronics, memory, spintronics, fuel cells, catalysis, gas storage, nanoparticle sizing and entrapment to name a few. The large surface to volume ratio of nanocolumn arrays should make possible very strong, robust materials for harsh environments (e.g., radiation and shock). Potential applications include the outer surface shielding of satellites and the inner wall of fusion energy systems. Coupling of laser energy into nanocolumn arrays is expected to produce a high yield of x-rays.

In this publication, we describe a method to produce uniform monodisperse nanocolumns and associated structures with a process inherently scalable to large commercial quantities: ion tracking lithography, etching and electrodeposition. The process is easily controlled to high tolerance and a very wide range of materials including semimetallic, ferromagnetic, nonferromagnetic, semiconducting, insulating and combinations of these materials, see table I. Independent control of nanocolumn diameter and areal density (columns/cm^2) allows for systematic study of a host of finite size effects. Defect structure and motion, mechanical properties, radiation effects, electrical, magnetic and optical effects (including at high field conditions) are all topics of great interest for the class of materials that can be formed by the method. All these materials can be formed by electroplating into nano pores, which are of interest in their own right. Thus, ion-track-formed pores have been used as a solution ion pump and as commercial filter media of unsurpassed quality.

Table 1. Examples of materials that can be electrodeposited

noble metals	Au, Ag, Cu, Pt
transition metals	Fe, Co, Ni
semimetals	Bi, In, Sb
semiconductors	CdS, ZnS
metal oxides	ZnO, TiO_2, Cu_2O
alloys	NiFe, FeCo, BiSb
electronically conducting polymers	polyaniline, polypyrrole, polythiophene

The large areas and great uniformity of our method open a wealth of possibilities in scientific investigation and technological implementation. Optical spectroscopy, diffraction, catalysis, electrical and magnetic measurements, and characterization by positrons will all benefit from the large signals of such structures. These materials can also be made to have properties ranging from oriented (anisotropic) to non-aligned (isotropic). For semiconductors and semimetals, the small diameter of the columns will create strong quantum confinement in two directions while their length facilitates the non-trivial task of injecting electrical and spin currents. These nanocolumn structures can also serve as a basis for more complicated structures such as those functionalized with organics, coated with additional layers, or passivated. Alternating layers of two or more materials are possible [4,5]. Small numbers of columns or even single columns lend themselves to other experiments such as direct TEM investigation without artifacts from sample preparation for structural characterization and mechanical properties.

The basic processes used are the same as those in the fabrication of flat panel displays [6] and in microelectronics, and this can speed the introduction of recent discoveries [7-10] into new materials and into modern technology and devices.

Fabrication of Nanocolumns

Columns as small as 5 nm in diameter and lengths as long as tens of microns appear readily possible with the technique. Diameter, length, and areal density are independently set and accurately controlled. The nanocolumns are produced by first wet etching tracks created by energetic ions and then filling the tracks by electro-deposition as shown schematically in figure 1.

The first step in the process is directing appropriate energetic ions through a layer of trackable material (generally a dielectric material) to create latent nuclear tracks, see Figure 1 A. A latent track is the cylindrical zone remaining around the essentially straight path of an energetic ion that deposited energy mainly via interactions with the electrons of the material. When the energy deposited exceeds a critical value each latent track consists of a continuous, cylindrical volume that has been modified leaving a lower density, chemically different material. The lower density results from the creation of vacancies, and the chemical modification results from the destruction of the pre-existing

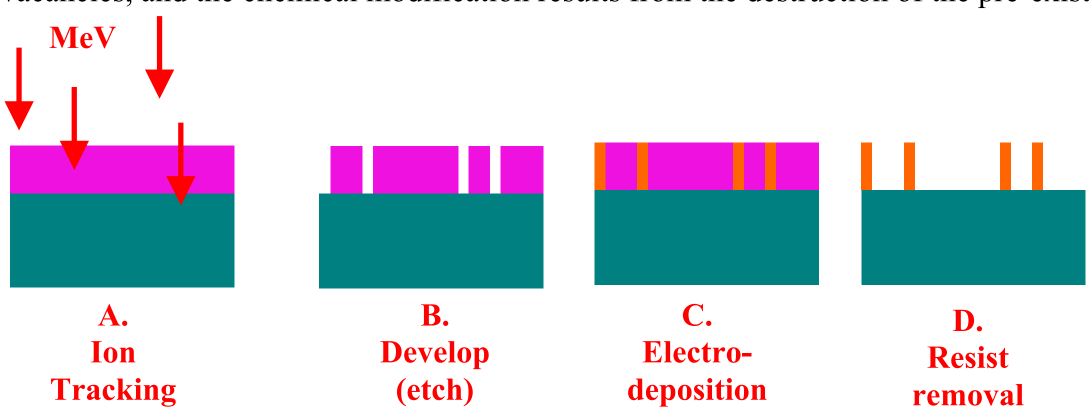

Figure 1. Process flow for formation of nanocolumns by ion tracking lithography. A. Energetic ions track medium (e.g. polycarbonate) that has been coated onto a substrate such as silicon with strike layer such as gold. B. Latent tracks developed, or etched, by potassium hydroxide solution forming monodisperse columnar holes. C. Metal, or other material, is electro-plated into holes. D. Track medium is removed by e.g. dissolution in KOH leaving freestanding random array of nanocolumns.

electronic bonding in the material. The diameter of the latent track depends on the energy density that the ion deposited into electronic stopping, which varies with the ion species, the ion energy, and the material, and is typically 5-30 nm. Polycarbonate, $[(OC_6H_4)C(CH_3)_2(C_6H_4O)C)]_n$, or more simply, $C_{16}H_{14}O_3$, as used in the present work, is commercially available as Lexan and Makrolon, and has been used as particle detectors and in tracking studies for over thirty years [11-15]. For polycarbonate the deposited energy due to electronic stopping results in chain scissions.

Next, the latent tracks are chemically etched to form nanopores or molds, see Figure 1 B. The diameter of the holes can be as small as a few nanometers or as large as several microns and is set by etchant concentration, temperature, and agitation, and of course by the time in contact with the solution. Materials such as polycarbonate, mica, and fused silica have been successfully used. Small holes in these materials are of interest in their own right in areas such as filtration, catalysis, and, recently, as a miniature pump of ions in solution [16]. Non-tracked polycarbonate is etched by cleavage of the carbonate linkage by hydroxide with hydrolysis of two adjacent carbonate linkages being required to release the relatively soluble bisphenolate anion from the surface [17]. The scissions in the tracks result in monomer segments at the end of a chain and require only one cleavage. This simpler process contributes to the higher etch rate in the track. In addition the etchant can diffuse faster into the track than into the non-tracked material. These effects qualitatively explain the much higher etch rate for the tracks than the base material and is the basis for making high aspect ratio holes.

To create nanocolumns of material, the pores are filled by an electrochemical deposition process. Thus, the trackable material must be a dielectric to allow the formation of the

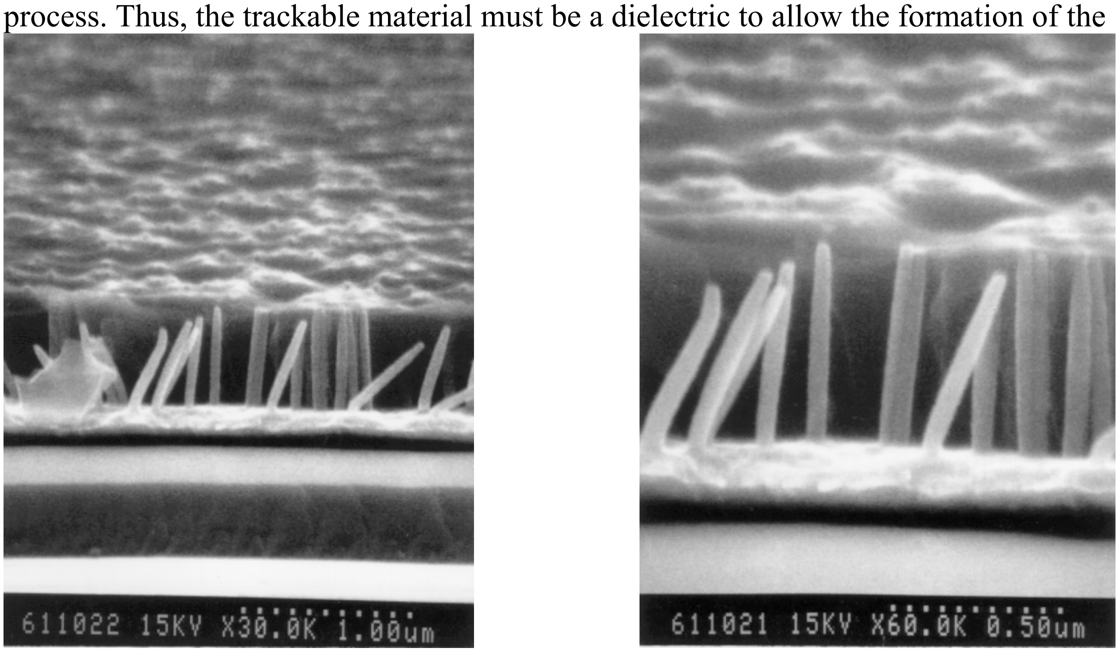

Figure 2. Section of a cleaved substrate containing nickel nanocolumns embedded in polycarbonate film. The polycarbonate has been torn off the substrate near the cleavage plane thereby exposing some nano columns. The deformation of the columns shows that they are firmly attached to the gold coated substrate and are malleable.

electrically conducting nanocolumns. Arrays of nanocolumn structures can be made by ion irradiation using a controlled dose, typically in the range, 10^6-10^{11} ions-cm^{-2}. For ions tracking at normal incidence, the maximum length of the nanocolumn can not, of course, exceed the thickness of the tracked layer. The actual length of the nanocolumns formed is proportional to the total charge transported during the deposition. The nanocolumns grow as the deposition material fills the pores in the template. Using this technique nanocolumns arrays can be created from any material that is amenable to electrodeposition. A key feature of templated electrodeposition is the ability to vary the composition along the length of the nanocolumn.[4,5]. For the present work, short, free-standing nickel nanocolumns [18] are fabricated conveniently using thin film techniques. Approximately 600-nm thick polycarbonate is spun onto a nickel-covered silicon wafer. Latent ion tracks with a density of ~10^8/cm^2 are created normal to the surface with 13.6 MeV Xe^{+4} ions from a Van de Graaff accelerator. The tracks are etched at ~300K with a solution of KOH to form ~80 nm diameter holes into which nickel is electroplated.

Results and Discussion

Although we have already published some results for nanocolumns, we now present previously unpublished figures, information and data. Figure 2 is a Scanning Electron Microscopy image of the polycarbonate/nickel nanowire composite. At the cleavage face

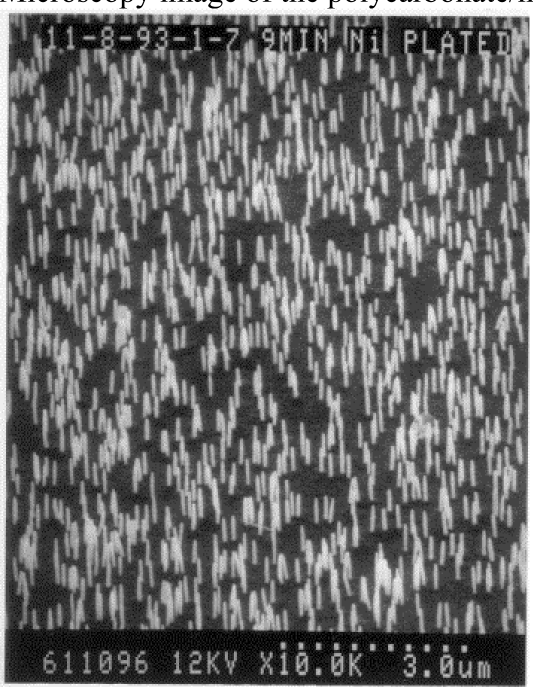

Figure 3. Electron micrographs of free-standing 80 nm diameter nickel nano-columns by the process described in figure 1. The nanocolumns are 600 nm tall and are distributed uniformly over very large areas in a random pattern Scale bar 3 micron. Strike layer: gold.

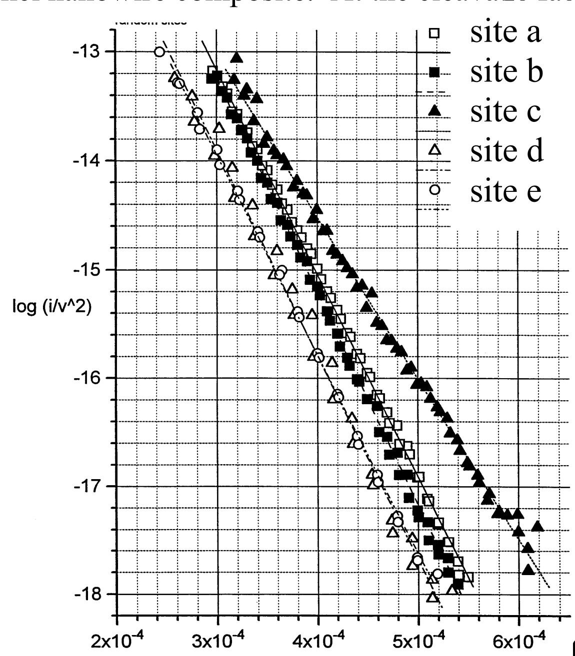

Figure 4. Electron field emission plot of an array similar to figure 3, except that it was composed of platinum nanocolumns on a gold coated silicon wafer. Similar response is found at the five locations measured indicating uniformity in the array across the wafer.

of the silicon wafer, polycarbonate has been forcefully removed revealing individual nanocolumns of nickel firmly attached to the gold-coated silicon substrate. The

nanocolumns are strongly bent by the rough removal technique, but remain firmly attached to the substrate. Removal of the mold by KOH results in the free-standing nanocolumn array shown in figure 3. A higher magnification image of this specimen can be found in reference 18.

An example of quantum behavior from such arrays is shown in figure 4. The straight-line behavior of the data on a Fowler-Nordheim plot indicates electron field emission, a quantum mechanical tunneling phenomenon. The silicon wafer was coated with a thin evaporated film of gold and the tracking, etching and electroplating process described above was used to form $2x10^7$ platinum nanowires per square centimeter. The field emission collector was a 100 micron diameter tungsten wire placed roughly 100 microns above the surface at five points across the wafer. Field emission is very sensitive to details of the shape and contamination of the emission tips. The relatively small difference among the five sites indicates excellent process control and uniformity.

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